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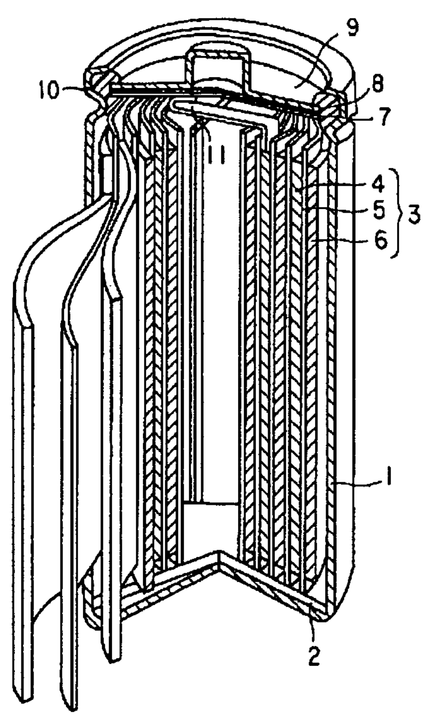
(54)【発明の名称】　非水溶媒二次電池の製造方法

(57)【要約】
【課題】　放電電圧が向上され、大電流充放電特性に優れ、かつ異常時の安全性が改善された非水溶媒二次電池を提供することを目的とする。
【解決手段】　リチウムイオンを吸蔵・放出する負極と、下記（１）式及び（２）式を満足するリチウムニッケル系複合酸化物を正極活物質として含む正極とを具備することを特徴とするものである。

$$0.75 \leq FWHM(003)/FWHM(104) \leq 0.9 \quad (1)$$

$$0.25 \leq I(104)/I(003) \leq 0.9 \quad (2)$$



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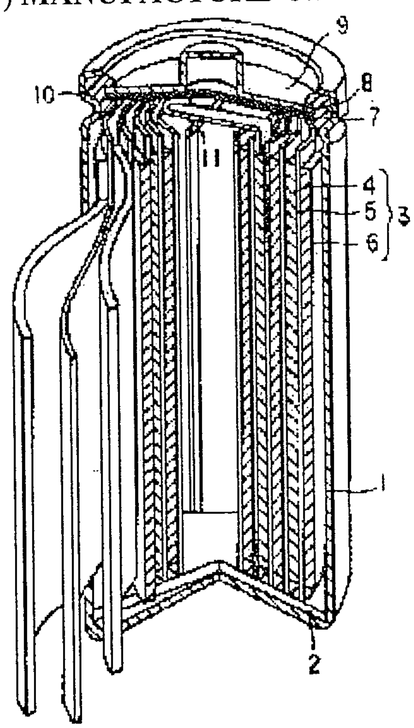
(54) MANUFACTURE OF NONAQUEOUS SOLVENT SECONDARY BATTERY



(57)Abstract:
PROBLEM TO BE SOLVED: To provide a nonaqueous solvent secondary battery that is improved in a discharge voltage, is excellent in a large-current charge-discharge characteristic and is improved in safety in an abnormal time.
SOLUTION: This nonaqueous solvent secondary battery is characterized by comprising a negative electrode capable of storing and releasing lithium ions, and a positive electrode containing, as a positive electrode active material, a lithium-nickel-based composite oxide satisfying the following inequalities (1) and (2). (1): $0.75 \leq FWHM(003)/FWHM(104) \leq 0.9$; (2): $0.25 \leq I(104)/I(003) \leq 0.9$.

CLAIMS

[Claim(s)]

[Claim 1] The non-aqueous-solvent rechargeable battery characterized by providing the positive electrode which contains the lithium nickel system multiple oxide with which it is [a lithium ion] satisfied of occlusion, the negative electrode to emit, and following the (1) type and (2) types as positive active material.

0.75 <=FWHM(003)/FWHM(104) <=0.9 (1)

0.25<=I (104) / I (003)<=0.9 (2)

However, the half peak width of the diffraction peak in the field in Miller indices hkl (003) of the powder X diffraction for which FWHM (003) used CuK alpha rays in (1) type, FWHM (104) shows the half peak width of the diffraction peak in the field in Miller indices hkl of the powder X diffraction which used CuK alpha rays (104). (2) In a formula, the integrated intensity of the diffraction peak in the field in Miller indices hkl (003) of the powder X diffraction for which I (003) used CuK alpha rays, and I (104) show the integrated intensity of the diffraction peak in the field in Miller indices hkl of the powder X diffraction which used CuK alpha rays (104).

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the non-aqueous-solvent rechargeable battery which improved positive active material.

[0002]

[Description of the Prior Art] In recent years, with small [of various kinds of electronic equipment, such as VTR, a cellular phone and a mobile computer,], and lightweight-izing, the demand of the rechargeable battery of a high energy consistency increases as those power sources, and research of the non-aqueous-solvent rechargeable battery which uses a lithium as a negative-electrode active material is done actively. It is already LiCoO2. The rechargeable lithium-ion battery used for positive active material is put in practical use as a rechargeable battery of a high energy consistency.

[0003] A non-aqueous-solvent rechargeable battery uses occlusion and the compound to emit for a negative electrode for a lithium, a lithium alloy, or a lithium ion. As the electrolytic solution, propylene carbonate (PC), ethylene carbonate (EC), Ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), Diethyl carbonate (DEC), 1, 2-dimethoxyethane (DME), gamma-butyl lactone (gamma-BL), a tetrahydrofuran (THF), the inside of non-aqueous solvents, such as 2-methyl tetrahydrofuran (2-MeTHF), -- LiClO4, LiBF4, LiAsF6, LiPF6, LiCF3 SO3, and LiAlCl4 etc. -- it consists of what dissolved lithium salt (electrolyte). Moreover, what contains the active material using the intercalation or doping phenomenon of a stratified compound as a positive electrode attracts attention.

[0004] As an example using the intercalation of said stratified compound, the

chalcogenide compound has the charge-and-discharge cycle property of having excelled comparatively. However, the chalcogenide compound had low electromotive force, and even when a lithium metal was used as a negative electrode, the practical charge electrical potential difference was before and after 2V at most, and was not what satisfies the point of the high electromotive force which is the description of a non-aqueous-solvent rechargeable battery.

[0005] V2 O5 which has the same layer structure on the other hand, and V6 -- O13, LiCoO2, and LiNiO2 Or LiMn 2O4 using a doping phenomenon etc. -- the metallic-oxide system compound attracts attention in that it has the description of high electromotive force. Especially, it is LiCoO2 and LiNiO2. The positive electrode included as an active material has about [4V] electromotive force, and, moreover, theoretical energy density has a big value of about 1 kWh/kg per positive active material.

[0006] However, LiNiO2 The non-aqueous-solvent rechargeable battery equipped with the positive electrode included as an active material has a low high current discharge property, and when abnormal current moreover flows according to overcharge by an inter-electrode short circuit, failure, incorrect actuation of charging equipment, etc. in the interior of a cell etc., in order that positive active material may pyrolyze, abnormality generation of heat of 300 degrees C or more is produced, nonaqueous electrolyte decomposes, internal pressure rises rapidly and it has a possibility may result in a burst or ignition.

[0007]

[Problem(s) to be Solved by the Invention] It is going to offer the non-aqueous-solvent rechargeable battery with which discharge voltage of this invention improved, and it excelled in the high current charge-and-discharge property, and the safety at the time of abnormalities has been improved.

[0008]

[Means for Solving the Problem] The non-aqueous-solvent rechargeable battery concerning this invention is characterized by providing the positive electrode which contains the lithium nickel system multiple oxide with which it is [a lithium ion] satisfied of occlusion, the negative electrode to emit, and following the (1) type and (2) types as positive active material.

[0009]

0.75 <=FWHM(003)/FWHM(104) <=0.9 (1)

0.25<=I (104) / I (003)<=0.9 (2)

However, the half peak width of the diffraction peak in the field in Miller indices hkl (003) of the powder X diffraction for which FWHM (003) used CuK alpha rays in (1) type, FWHM (104) shows the half peak width of the diffraction peak in the field in Miller indices hkl of the powder X diffraction which used CuK alpha rays (104). (2) In a formula, the integrated intensity of the diffraction peak in the field in Miller indices hkl (003) of the powder X diffraction for which I (003) used CuK alpha rays, and I (104) show the integrated intensity of the diffraction peak in the field in Miller indices hkl of the powder X diffraction which used CuK alpha rays (104).

[0010]

[Embodiment of the Invention] Hereafter, the non-aqueous-solvent rechargeable battery (for example, cylindrical shape non-aqueous-solvent rechargeable battery) concerning this invention is explained with reference to drawing 1 .

[0011] For example, as for the container 1 of the shape of a closed-end cylinder which consists of stainless steel, the insulator 2 is arranged at the pars basilaris ossis occipitalis. The electrode group 3 is contained in said container 1. Said electrode group 3 has structure which wound around the curled form the band-like object which carried out the laminating of a positive electrode 4, a separator 5, and the negative electrode 6 in this sequence.

[0012] Nonaqueous electrolyte is held in said container 1. Caulking immobilization of the positive-electrode terminal 9 of the hat configuration arranged at the relief valve 8 arranged on the PTC component 7 by which opening of the hole was carried out to the center section, and said PTC component 7, and said relief valve 8 is carried out through the insulating gasket 10 at up opening of said container 1. In addition, opening of the gas drainage hole (not shown) is carried out to said positive-electrode terminal 9. The end of the positive-electrode lead 11 is connected to said positive electrode 4, and the other end is connected to said PTC component 7, respectively. Said negative electrode 6 is connected to said container 1 which is a negative-electrode terminal through the negative-electrode lead which is not illustrated.

[0013] Next, said positive electrode 4, said separator 5, said negative electrode 6, and said nonaqueous electrolyte are explained in detail.

[0014] 1) a positive electrode 4 -- this positive electrode contains the positive active material which consists of a lithium nickel system multiple oxide with which are satisfied of following the (1) type and (2) types.

[0015]

0.75 <=FWHM(003)/FWHM(104) <=0.9 (1)

However, in (1) type, the half peak width of the diffraction peak in the field in Miller indices hkl (003) of the powder X diffraction for which FWHM (003) used CuK alpha rays, and FWHM (104) show the half peak width of the diffraction peak in the field in Miller indices hkl of the powder X diffraction which used CuK alpha rays (104).

[0016]

0.25<=I (104) / I (003)<=0.9 (2)

However, in (2) types, the integrated intensity of the diffraction peak in the field in Miller indices hkl (003) of the powder X diffraction for which I (003) used CuK alpha rays, and I (104) show the integrated intensity of the diffraction peak in the field in Miller indices hkl of the powder X diffraction which used CuK alpha rays (104).

[0017] The multiple oxide which permuted the multiple oxide which permuted some nickel of LiNiO2 and LiNiO2 by the element, the nickel of LiNiO2, and a part of oxygen by the element as a lithium nickel system multiple oxide can be mentioned.

[0018] As a multiple oxide which permuted some nickel of LiNiO2 by the element, the multiple oxide by which an empirical formula is expressed with LiNi1-x Mx O2 (however, M is an element more than a kind as being chosen from Co, Mn, B, aluminum, and Li as it is few, and the range of an atomic ratio x is 0< x<=0.5) is desirable. The multiple oxide expressed with said empirical formula includes what uses only Li as M, i.e., the thing expressed with Li1+y nickel1-y O2 (however, the range of an atomic ratio y is 0< y<=0.1). As for M, it is more desirable that they are Co, Mn, and aluminum.

[0019] Specifying in said range depends an atomic ratio x on the following reasons. If an atomic ratio x exceeds 0.5, since it will become easy to mix nickel ion to a lithium ion site, there is a possibility that the active material with which are satisfied of the above (1)

and (2) types may no longer be obtained. The more desirable range of an atomic ratio x is 0.1<=x<=0.3.

[0020] Specifying in said range depends an atomic ratio y on the following reasons. If an atomic ratio y exceeds 0.1, since the crystal structure will become unstable, there is a possibility that sufficient charge-and-discharge cycle property may no longer be acquired. The more desirable range of an atomic ratio y is 0.01<=y<=0.05.

[0021] As a multiple oxide which permuted the nickel of LiNiO2, and a part of oxygen by the element, the multiple oxide expressed with Li1+z nickel1-x-z MxO2-z Fz (however, the range of an atomic ratio x is 0< x<=0.5, and the range of an atomic ratio z is 0< z<=0.25) is desirable.

[0022] Specifying in said range depends an atomic ratio x on the following reasons. If an atomic ratio x exceeds 0.5, since it will become easy to mix nickel ion to a lithium ion site, there is a possibility that the active material with which are satisfied of the above (1) and (2) types may no longer be obtained. The more desirable range of an atomic ratio x is 0.1<=x<=0.3.

[0023] Specifying in said range depends an atomic ratio z on the following reasons. Since diffusion of a lithium ion may be barred even if the active material has satisfied the conditions of the aforementioned (1) formula and (2) types when an atomic ratio z exceeds 0.25, a high charge-and-discharge capacity may not be obtained. The more desirable range of an atomic ratio z is 0< z<=0.1.

[0024] As for the average valence of the nickel in said positive active material, it is desirable that it is [or more 2.9] 3.1 or less. This is based on the following reasons. If the average valence of nickel is made less than into 2.9, since the amount of nickel of the bivalence under crystal will increase, there is a possibility that it may become difficult to acquire sufficient discharge capacity and a high current discharge property. That is, since the work which maintains the charge under crystal at neutrality will arise if the nickel of about [barring diffusion of the lithium ion accompanying charge and discharge, since it is easy to mix the nickel of bivalence in a lithium site], and bivalence exists, the amount of lithium ions in which occlusion and emission are possible decreases. For this reason, there is a possibility that it may become impossible to acquire sufficient discharge capacity and a high current discharge property. On the other hand, if the average valence of nickel exceeds 3.1, the deficit of a lithium may have arisen. If the deficit of a lithium arises, in order that the amount of lithium ions in which occlusion and emission are possible may decrease, there is a possibility that it may become impossible to acquire sufficient discharge capacity and a high current discharge property. The more desirable range of the average valence of nickel is 3.05 or less [2.95 or more].

[0025] The crystal structure of a lithium nickel system multiple oxide is the layer structure, and belongs to trigonal system. Occlusion and emission of a lithium ion are done from the direction which intersects perpendicularly with the c-axis of trigonal system. The field in Miller indices hkl of the powder X diffraction using CuK alpha rays (003) is related in the direction of a c-axis of trigonal system. On the other hand, the field in Miller indices hkl of the powder X diffraction using CuK alpha rays (104) is related in the direction which intersects perpendicularly with the c-axis of trigonal system.

[0026] (1) Specifying in said range depends FWHM (003)/FWHM (104) in a formula on the following reasons. If FWHM (104) exceeds FWHM (003)/0.9, the c-axis stacking tendency of trigonal system will be low (the crystal growth to the direction of a c-axis is

inadequate), and, moreover, a lot of nickel ion will mix to the lithium ion site. Such an active material has the trouble of explaining to the following (a) - (c).

[0027] (a) Since the c-axis stacking tendency of trigonal system is low, when a crystal grows in the direction perpendicular to a c-axis, the spreading diffusion distance of a lithium ion becomes long.

(b) If it becomes the crystal structure with many disorders of nickel ion, the valence of nickel ion will become less than three. Consequently, since the work which maintains **** under crystal at neutrality arises, the amount of lithium ions in which occlusion and emission are possible decreases.

(c) The nickel ion mixed to the lithium ion site prevents a lithium ion from being spread in an active material.

[0028] Therefore, in order that reaction resistance of the active material at the time of charge and discharge may become high and lithium ion occlusion and a burst size may moreover decrease, discharge potential falls and a high current discharge property falls. Moreover, since the active material with the high reaction resistance at the time of charge and discharge produces a pyrolysis at low temperature, it causes a rapid temperature rise at the time of abnormalities.

[0029] If FWHM (003)/FWHM (104) becomes small, the c-axis stacking tendency of trigonal system will become high, and although there is an inclination for the disorder of nickel ion to decrease, it becomes that in which the crystal growth to a direction perpendicular to a c-axis was inferior in FWHM (003)/FWHM (104) being less than 0.75 as compared with the crystal growth to the direction of a c-axis. It is checked that expansion and contraction of the crystal accompanying a charge-and-discharge reaction take place along a c-axis and the direction of an a-axis. The occlusion from the direction where a c-axis and a lithium ion cross at right angles, and since it is emitted, expansion / contraction degree of the direction of a c-axis becomes large compared with the direction of an a-axis. If the crystal growth to the direction of a c-axis is relatively large, since much expansion and contraction of the direction of a c-axis where a degree from the first is large will be accumulated, expansion / contraction degree of an active material becomes remarkably large, and a cycle property falls. The more desirable range of FWHM (003)/FWHM (104) is 0.8 <=FWHM(003)/FWHM(104) <=0.85.

[0030] (003) As for the half peak width FWHM of the diffraction peak of a field (003), it is desirable to make it the range of 0.1 degree<=FWHM(003) <=0.16 degree. By making it said range, discharge capacity and discharge potential can be improved further. It is 0.12 degree<=FWHM(003) <=0.15 degree more preferably.

[0031] (104) As for the half peak width FWHM of the diffraction peak of a field (104), it is desirable to make it the range of 0.13 degree<=FWHM(104) <=0.2 degree. By making it this range, the crystal growth to a direction perpendicular to the c-axis of trigonal system can be controlled, and the stacking tendency of a c-axis can be moderately made high. It is 0.14 degree<=FWHM(104) <=0.18 degree more preferably.

[0032] (2) Specifying in said range depends I (104)/I (003) in a formula on the following reasons. If I (003) exceeds I (104)/0.9, a lot of nickel ion will mix to a lithium ion site. Consequently, since reaction resistance of the active material at the time of charge and discharge becomes high while the amount of lithium ions in which occlusion and emission are possible decreases, discharge potential becomes low and a high current charge-and-discharge property falls. If I (104)/I (003) of that whose disorder of nickel ion

will decrease if I (104)/I (003) is made small is made less than into 0.25, an active material and the electrolytic solution will become easy to react. As for I (104)/I (003), it is more desirable to make it 0.25<=I (104) / the range of I (003)<=0.8.

[0033] As for said positive active material, it is desirable that the volume accumulation frequency 10 of the particle size distribution of an aggregated particle and 50 or 90% of particle size D10, D50, and D90 fill 0.3 <=(D10/D50) <=0.8 and 1 <=(D90/D50) <=3. This is based on the following reasons. When D10/D50 are less than 0.3, it means that many minute particles are contained. When there are many minute particles, there is a possibility that a cycle property may fall remarkably. Moreover, since the fill of an active material decreases when D10/D50 exceed 0.8, and D90/D50 are less than one, and an electrode is produced also in any in case D90/D50 exceed 3, there is a possibility that the discharge capacity as a cell may decrease. As for D10, D50, and D90, it is more desirable to fill 0.4 <=(D10/D50) <=0.7 and 1.2 <=(D90/D50) <=2.5.

[0034] When filling the specific relation which D10, D50, and D90 mentioned above, as for said D50, it is desirable that it is [0.2 micrometer or more] 50 micrometers or less. This is based on the following reasons. When D50 is less than 0.2 micrometers, crystal growth becomes inadequate and there is a possibility that it may become impossible to obtain sufficient discharge capacity. On the other hand, when D50 exceeds 50 micrometers, in case an electrode is produced, it may become difficult to acquire a uniform electrode surface. The more desirable range of D50 is 1 micrometers or more 25 micrometers or less.

[0035] As for the specific surface area of said positive active material, it is desirable that they are 0.2-2m2 / g. If said specific surface area is made into under 0.2m2 / g, the touch area of said positive active material and electrolytic solution will decrease, and sufficient discharge capacity will no longer be obtained. Furthermore, there is a possibility that charge-and-discharge effectiveness may fall by reduction of reaction area. On the other hand, if said specific surface area exceeds 2m2 / g, the decomposition reaction of the electrolytic solution will become easy to occur with the increment in reaction area, the decomposition reaction of positive active material will advance by the reaction of positive active material and the electrolytic solution further, and it will become easy to cause the condition of having called it abnormality generation of heat, and a burst and ignition of a cell at the time of the abnormalities in a cell including overcharge. The more desirable range of specific surface area is below 1.5m2 / g more than 0.3m2/g.

[0036] Said positive active material is produced by the approach explained below.

[0037] (The 1st process) A raw material compound is mixed so that it may become a predetermined mole ratio, this is distributed in organic solvents, such as aqueous intermediation, aqueous acids, an alkaline water solution or a methanol, ethanol, and an acetone, and spray drying of the obtained slurry is carried out.

[0038] If a raw material compound is once distributed in a solvent and spray drying of this is carried out, it will become possible mixing a raw material compound to homogeneity rather than mixing the raw material compound of a solid state.

[0039] As a raw material compound, nickel hydroxide [nickel (OH)2] and nickel carbonate (NiCO3), The nickel compound of nickel oxide (NiO), nickel nitrate [nickel (NO3)2], etc., A lithium hydroxide (LiOH), lithium oxide (Li2O), a lithium carbonate (Li2 CO3), Lithium halide salts, such as lithium compounds, such as a lithium nitrate (LiNO3), and lithium fluoride (LiF), Cobalt hydroxide [Co (OH)2] and cobalt carbonate

($CoCO_3$), The cobalt compound of cobalt oxide (CoO and Co $2O_3$), a cobalt nitrate [Co $(NO_3)_2$], etc., The manganese compound of manganese oxide (MnO_2), manganese carbonate ($MnCO_3$), manganese nitrate [Mn $(NO_3)_2$], etc., A boric acid (H_3 BO_3), a tetraboric-acid lithium (Li_2 B_4 O_7), Boron compounds, such as boron oxide (B-2 O_3) and $LiBH_4$ ($LiBH_4$), An aluminum hydroxide [aluminum $(OH)_3$] and an aluminum oxide (aluminum $2O_3$), The aluminium compound of an aluminum sulfate [aluminum2 3 (SO_4)], an aluminium nitrate [aluminum $(NO_3)_3$], etc., At least one kind of element chosen from Co, Mn, and aluminum can mention what covered the front face of the nickel hydroxide by which coprecipitation was carried out with the hydroxide of at least one kind of element chosen from Co, Mn, and aluminum.
[0040] Moreover, when compounding the multiple oxide which permuted the multiple oxide which permuted some nickel of $LiNiO_2$ by the element, the nickel of $LiNiO_2$, and a part of oxygen by the element, $LiNiO_2$ can be used as a raw material compound.
[0041] (The 2nd process) An oxygen density carries out maintenance (baking) of said raw material compound at 650-750 degrees C in 18 - 100% of oxidizing atmosphere for 5 hours or more.
[0042] Said oxidizing atmosphere may contain argon gas and inert gas like nitrogen gas. When an oxygen density is made less than 18%, there is a possibility that unreacted products, such as a lithium carbonate and nickel oxide, may remain so much on the surface of an active material. An unreacted product causes the fall of about [that a lithium ion checks occlusion and being emitted to an active material] and discharge potential. Since an unreacted product can be reduced and mixing of the nickel ion to a lithium ion site can be controlled by making the oxygen density of an oxidizing atmosphere 18% or more, the active material with which are satisfied of the aforementioned (1) formula and (2) types can be obtained.
[0043] Specifying retention temperature in said range is based on the following reasons. If it is made lower than 650 degrees C, in order that reacting may become inadequate, an unreacted product may remain so much and a lot of nickel ion may moreover mix to a lithium ion site, there is a possibility that the active material with which are satisfied of the aforementioned (1) formula and (2) types may no longer be obtained. On the other hand, if it exceeds 750 degrees C, since the desorption of oxygen will happen by the decomposition reaction, there is a possibility that the very high nickel oxide of reaction resistance may adhere to an active material front face mostly. Nickel oxide becomes the factor which checks the occlusion and release reaction of a lithium ion.
[0044] (The 3rd process) The oxygen density pressurized by 0.1 - 50MPas performs heat treatment in 18 - 100% of oxidizing atmosphere for 1 hour or more at 450 (as oxygen tension, it is 0.018 or more-MPas 50 or less MPas)-900 degrees C.
[0045] It is controllable by this process on the level aiming at the c-axis stacking tendency in a crystal structure.
[0046] Said oxidizing atmosphere may contain argon gas and inert gas like nitrogen gas. Moreover, as for the oxygen density in an ambient atmosphere, it is desirable to be specified in said range for the reason same with having mentioned above.
[0047] Specifying heat treatment temperature in said range is based on the following reasons. If it is made lower than 450 degrees C, since crystal growth and the rearrangement of a crystal are very late, it will become difficult to acquire the crystal structure which has the half peak width for which it asks. On the other hand, if it exceeds

900 degrees C, although crystal growth and the rearrangement of a crystal will advance, a deoxidation reaction occurs in a particle front face, and there is a possibility of producing a high resistive layer.
[0048] Specifying the pressure of a heat treatment ambient atmosphere in said range is based on the following reasons. If it heat-treats by 0.1 or less MPases, since a deoxidation reaction will tend to occur, there is a possibility that nickel oxide and the lithium carbonate which check the occlusion and emission of a lithium ion may remain so much. On the other hand, if it heat-treats by 50 or more MPases, since distortion will arise into a crystal, a charge-and-discharge cycle may follow on going on, and may attract structure degradation.
[0049] (The 4th process) It cools slowly at the rate of 50 degrees C [or less]/h.
[0050] If a cooling rate exceeds 50 degrees C/h, since mixing of the nickel ion to a lithium ion site will become easy to take place, there is a possibility that the active material with which are satisfied of the aforementioned (1) formula and (2) types may no longer be obtained. By making a cooling rate into 50 degrees C [or less]/h, mixing of the nickel ion to a lithium ion site can be controlled, and the order ring of the layer structure can be raised.
[0051] the mixture which said positive electrode suspended positive active material, the electric conduction agent, and the binder in the suitable solvent, and was obtained -- it is produced by judging in the magnitude which asks for what applied the slurry to the charge collector, was dried and was made into the shape of sheet metal. At this time, it is the coverage of one side 100 - 400 g/m2 It is desirable to make it the range. Moreover, said positive electrode may be produced by sticking on kneading the pellet which fabricated positive active material with the electric conduction agent and the binder, or positive active material, and sticking on said charge collector what was sheet-ized with an electric conduction agent and a binder.
[0052] As said electric conduction agent, acetylene black, carbon black, a graphite, etc. can be raised, for example.
[0053] As said binder, for example Polyvinylidene fluoride (PVdF), A vinylidene fluoride-6 fluoride propylene copolymer, a vinylidene fluoride-tetrafluoroethylene-6 fluoride [propylene] ternary polymerization object, A vinylidene fluoride-pentafluoropropylene copolymer, a vinylidene fluoride-chlorotrifluoroethylene copolymer, A tetrafluoroethylene-vinylidene fluoride copolymer, a tetrafluoroethylene-perfluoroalkyl vinyl ether (PFA)-vinylidene fluoride ternary polymerization object, A tetrafluoroethylene-hexafluoropropylene (FEP)-vinylidene fluoride ternary polymerization object, A tetrafluoroethylene-ethylene-vinylidene fluoride ternary polymerization object, A chlorotrifluoroethylene-vinylidene fluoride copolymer, a chlorotrifluoroethylene-ethylene-vinylidene fluoride ternary polymerization object, A vinyl fluoride-vinylidene fluoride copolymer, ethylene-propylene-diene copolymer (EPDM) A styrene butadiene rubber (SBR) etc. can be used.
[0054] the blending ratio of coal of said positive active material, an electric conduction agent, and a binder -- 80 - 95 % of the weight of positive active material, and an electric conduction agent -- it is desirable that it is the range of 2 - 10 % of the weight of binders three to 20% of the weight.
[0055] As said charge collector, although aluminium foil, a stainless steel foil, a titanium foil, etc. can be used, for example, when tensile strength, electrochemical stability, the

flexibility at the time of winding, etc. are taken into consideration, aluminium foil is the most desirable. As thickness of the foil at this time, it is desirable that it is [10 micrometer or more] 30 micrometers or less.

[0056] 2) As the negative-electrode 6 aforementioned negative electrode 6, what contains occlusion and the compound to emit for a lithium ion is desirable.

[0057] The carbon material which consists of an organic substance sintered compact which can dope conductive polymers, such as polyacetal which can dope a lithium ion for said lithium ion as occlusion and a compound to emit, for example, polyacethylene, and polypyrrole, and a lithium ion can be raised.

[0058] Said carbon material changes in a property fairly with the raw material and calcinating methods. For example, graphite system carbon material, carbon material in which the graphite crystal section and the amorphism section were intermingled, the carbon material which takes the random layer structure which does not have regularity in the laminating of a crystal layer can be raised.

[0059] said negative electrode -- for example, the compound and binder which do occlusion and emission of said lithium ion -- a suitable solvent -- suspending -- this mixture -- it is produced by judging in the magnitude which asks for what applied the slurry to the charge collector, was dried and was made into the shape of sheet metal. At this time, it is the coverage of one side 50 - 200 g/m2 It is desirable to make it the range. Moreover, occlusion and the compound to emit may be stuck on kneading, what was sheet-ized may be stuck on said charge collector for the pellet which fabricated occlusion and the compound to emit for said lithium ion with the binder, or said lithium ion with a binder, and said negative electrode may be produced.

[0060] The positive electrode mentioned above having explained as said binder and the same thing can be used.

[0061] As for the blending ratio of coal of said negative-electrode ingredient and a binder, it is desirable that it is the range of 80 - 98 % of the weight of negative-electrode ingredients and 2 - 20 % of the weight of binders.

[0062] As said charge collector, although copper foil, a nickel foil, etc. can be used, for example, when electrochemical stability, the flexibility at the time of winding, etc. are taken into consideration, copper foil is the most desirable. As thickness of the foil at this time, it is desirable that it is [8 micrometer or more] 20 micrometers or less.

[0063] 3) The nonaqueous electrolyte aforementioned nonaqueous electrolyte has the presentation which dissolved the electrolyte in the non-aqueous solvent.

[0064] As said non-aqueous solvent, one sort or two sorts or more of mixture chosen, for example from propylene carbonate (PC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), 1, 2-dimethoxyethane (DME), diethoxy ethane (DEE), gamma-butyrolactone (gamma-BL), tetrahydrofuran (THF), 2-methyl tetrahydrofuran (2-MeTHF), 1, 3-dioxolane, 1, and 3-dimethoxypropane can be raised.

[0065] As said electrolyte, one sort or two sorts or more of lithium salt chosen, for example from lithium perchlorate (LiClO4), hoe lithium fluoride (LiBF4), a 6 fluoride arsenic lithium (LiAsF6), a 6 phosphorus-fluoride acid lithium (LiPF6), a truffe RUROMETA sulfonic-acid lithium (LiCF3 SO3), and an aluminum tetrachloride lithium (LiAlCl4) can be raised. As for the amount of dissolutions to said non-aqueous solvent of said electrolyte, it is desirable to make it 0.5-1.5 mols / L.

[0066] The non-aqueous-solvent rechargeable battery concerning this invention explained in full detail above is equipped with the positive electrode which contains the lithium nickel system multiple oxide with which are satisfied of (1) type and (2) types which were mentioned above as positive active material. Such an active material has the moderately high c-axis stacking tendency of trigonal system, and it has the crystal structure of the shape of a layer by which mixing of the nickel ion to a lithium ion site was controlled. Since said active material can diffuse the lithium ion accompanying a charge-and-discharge reaction easily and promptly while being able to make the amount of lithium ions in which occlusion and emission are possible increase, it can reduce reaction resistance of charge-and-discharge reaction time. Consequently, since the rechargeable battery equipped with the positive electrode containing said active material can make discharge potential high, it can improve a high current discharge property. Since it can control that a pyrolysis arises in positive active material when an internal short circuit arises in the state of charge in coincidence or abnormal current flows [overcharging by failure, incorrect actuation, etc. of charging equipment, etc. and], a rapid temperature rise can be avoided and a burst and ignition can be prevented.
[0067] It is LiNi1-x Mx O2 (however, it Co(es) M) about the presentation of said positive active material. As being chosen from Mn, B, aluminum, and Li, it is an element more than a kind as it is few. an atomic ratio x -- the range of 0< x<=0.5 -- it is -- by making it what makes it what is expressed or is expressed with Li1+y nickel1-y O2 (however, the range of an atomic ratio y is 0< y<=0.1) Since too much crystal structure change accompanying a charge-and-discharge reaction can be controlled, the charge-and-discharge cycle life of a rechargeable battery can be improved. Moreover, since the specific surface area in an aggregated particle front face in case said positive active material takes the gestalt of an aggregated particle can be reduced, the decomposition reaction of the nonaqueous electrolyte on the front face of an active material can be controlled.
[0068] In addition, the positive electrode which contains the lithium nickel system multiple oxide with which are satisfied of (1) type and (2) types which were mentioned above as positive active material, A 3 electrode glass cell is assembled using the counter electrode and reference pole which consist of a metal lithium. Charge-and-discharge cycle trial (it carries out by the constant current of 1 mA/cm2 to 4.2V) [Charge;] Carry out after reaching 4.2V until a current becomes 1/10 or less by the constant voltage. discharge; -- until it reaches 3V by the constant current of 1 mA/cm2 -- carrying out -- after 50 cycle ****** When the positive electrode was taken out from the glass cell and the powder X diffraction using CuK alpha rays was carried out, the range of the peak intensity ratios I (104)/I (003) was 0.25-0.4, and the range of the half-peak-width ratios FWHM (003)/FWHM (104) was 0.75-0.9.
[0069]
[Example] Hereafter, the example of this invention is explained to a detail with reference to a drawing.
Spray drying was performed after having been dropped so that the mole ratio of Li:nickel might become [example 1] nickel hydroxide powder with 1.02:1 about the lithium-hydroxide water solution of 3 mol/L, and fully mixing. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. The oxygen air current was

introduced for the obtained product, and as the oxygen density became 95% or more, after it held, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.
[0070] A presentation is $LiNiO_2$ when the powder X diffraction which used CuK alpha rays was carried out about the obtained product. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said $LiNiO_2$ Powdered D50 and specific surface area are shown in the following table 2.
[0071] subsequently, said $LiNiO_2$ after mixing powder and mixing 5 % of the weight of acetylene black with a ball mill 90% of the weight for 1 hour, while making it dissolve in N-methyl pyrrolidone so that polyvinylidene fluoride may become 5 % of the weight, keeping temperature at 10 degrees C and keeping humidity to 20% or less -- a mixture -- the slurry was prepared. this mixture -- it applied and dried, the roll press of the slurry was carried out to aluminium foil, and the positive electrode was produced.
[0072] Moreover, the mesophase pitch based carbon fiber was graphitized at 3000 degrees C under the argon gas ambient atmosphere, it heat-treated under the 2400 more-degree C chlorine gas ambient atmosphere, and graphitized-carbon powder was compounded. then, 94 % of the weight of said graphitized-carbon powder and 6 % of the weight of polyvinylidene fluorides are dissolved in N-methyl pyrrolidone -- making -- a mixture -- the slurry was prepared. this mixture -- it applied and dried, the roll press of the slurry was carried out to copper foil, and the negative electrode was produced.
[0073] After carrying out the laminating of the separator which consists of said positive electrode and a fine porosity film made from polypropylene, and said negative electrode in this sequence, respectively, the winding electrode group was produced to the curled form so that said negative electrode might serve as the outermost periphery.
[0074] Furthermore, it is $LiPF_6$ to the mixed solvent (rate 1:2 of a mixed volume ratio) of ethylene carbonate and ethyl methyl carbonate. Nonaqueous electrolyte was prepared by doing 1.0 mols / L dissolution of.
[0075] Said electrode group and said nonaqueous electrolyte were contained in the closed-end cylindrical cup made from stainless steel, and the cylindrical non-aqueous-solvent rechargeable battery of the structure shown in drawing 1 mentioned above by giving obturation etc. was assembled.
[0076] [Example 2] nickel0.83Co0.17 (OH) 2 Spray drying was performed after having been dropped so that the mole ratio of Li: (nickel+Co) might become the cobalt coprecipitation nickel hydroxide powder expressed with 1.02:1 about the lithium-hydroxide water solution of three mols / L, and fully mixing. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. As the oxygen density became 95% or more, after it introduced the oxygen air current, and it held the obtained product, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.
[0077] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is $LiNi_{0.83}Co_{0.17}O_2$. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said $LiNi_{0.83}Co_{0.17}O_2$ Powdered D50 and specific surface area are

shown in the following table 2.

[0078] Obtained LiNi0.83Co 0.17O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.

[0079] [Example 3] nickel0.83Co0.17 (OH) 2 The cobalt coprecipitation nickel hydroxide powder expressed was distributed so that the mole ratio of aluminum: (nickel+Co) might be set to 0.02:1 in the aluminium nitrate water solution of 3 mol/L. The sodium-hydroxide water solution of 3 mol/L is dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C. Spray drying was performed after having been dropped so that the mole ratio of Li: (nickel+Co+aluminum) might become the obtained product with 1.02:1 about the lithium-hydroxide water solution of 3 mol/L, and fully mixing. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. As the oxygen density became 95% or more, after it introduced the oxygen air current, and it held the obtained product, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.

[0080] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.81Co0.17aluminum 0.02O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.81Co0.17aluminum 0.02O2 Powdered D50 and specific surface area are shown in the following table 2.

[0081] Obtained LiNi0.81Co0.17aluminum 0.02O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.

[0082] [Example 4] nickel0.83Co0.17 (OH) 2 The cobalt coprecipitation nickel hydroxide powder and aluminum hydroxide which are expressed were distributed so that the mole ratio of aluminum: (nickel+Co) might become the aluminium nitrate water solution of one mol / L with 0.003:1. The sodium-hydroxide water solution of 3 mol/L was dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C, and the front face was covered with the aluminum hydroxide. Spray drying was performed after having been dropped so that the mole ratio of Li: (nickel+Co+aluminum) might become the obtained product with 1.02:1 about the lithium-hydroxide water solution of 3 mol/L, and fully mixing. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. As the oxygen density became 95% or more, after it introduced the oxygen air current, and it held the obtained product, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.

[0083] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.827 Co0.17aluminum 0.003O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.827 Co0.17aluminum

0.003O2 Powdered D50 and specific surface area are shown in the following table 2.
[0084] Obtained LiNi0.827 Co0.17aluminum 0.003O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.
[0085] [Example 5] nickel0.83Co0.17 (OH) 2 The cobalt coprecipitation nickel hydroxide powder and aluminum hydroxide which are expressed were distributed so that the mole ratio of aluminum: (nickel+Co) might become the aluminium nitrate water solution of one mol / L with 0.003:1. The sodium-hydroxide water solution of 3 mol/L was dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C, and the front face was covered with the aluminum hydroxide. Spray drying was performed after having been dropped so that the mole ratio of Li: (nickel+Co+aluminum) might become the obtained product with 1.02:1 about the lithium-hydroxide water solution of 3 mol/L, and fully mixing. It held at the temperature of 710 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. As the oxygen density became 95% or more, after it introduced the oxygen air current, and it held the obtained product, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.
[0086] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.827 Co0.17aluminum 0.003O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.827 Co0.17aluminum 0.003O2 Powdered D50 and specific surface area are shown in the following table 2.
[0087] Obtained LiNi0.827 Co0.17aluminum 0.003O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.
[0088] [Example 6] nickel0.83Co0.17 (OH) 2 The cobalt coprecipitation nickel hydroxide powder and aluminum hydroxide which are expressed were distributed so that the mole ratio of aluminum: (nickel+Co) might become the aluminium nitrate water solution of one mol / L with 0.003:1. The sodium-hydroxide water solution of 3 mol/L was dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C, and the front face was covered with the aluminum hydroxide. Spray drying was performed after having been dropped so that the mole ratio of Li: (nickel+Co+aluminum) might become the obtained product with 1.02:1 about the lithium-hydroxide water solution of 3 mol/L, and fully mixing. It held at the temperature of 700 degrees C for 5 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. As the oxygen density became 95% or more, after it introduced the oxygen air current, and it held the obtained product, heat-treatment was performed at 600 degrees C for 5 hours, pressurizing to 1MPas.
[0089] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.827 Co0.17aluminum 0.003O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the

values shown in the following table 1. Moreover, said LiNi0.827 Co0.17aluminum 0.003O2 Powdered D50 and specific surface area are shown in the following table 2.
[0090] Obtained LiNi0.827 Co0.17aluminum 0.003O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.
[0091] [Example 7] nickel hydroxide powder was distributed so that the mole ratio of Mn:nickel might become the manganese nitrate water solution of 3 mol/L with 1:4. The sodium-hydroxide water solution of 3 mol/L is dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C. Spray drying was performed after having been dropped so that the mole ratio of Li: (nickel+Mn) might become the obtained product with 1.02:1 about the lithium-hydroxide water solution of 3 mol/L, and fully mixing. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. The oxygen air current was introduced for the obtained product, and as the oxygen density became 95% or more, after it held, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.
[0092] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.8 Mn 0.2O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.8 Mn 0.2O2 Powdered D50 and specific surface area are shown in the following table 2.
[0093] Obtained LiNi0.8 Mn 0.2O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.
[0094] Spray drying was performed after having distributed [example 8] nickel hydroxide powder and lithium fluoride so that the mole ratio of Li:nickel:F might become the lithium-hydroxide water solution of 3 mol/L with 1.05:0.95:0.05, and mixing enough. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. The oxygen air current was introduced for the obtained product, and as the oxygen density became 95% or more, after it held, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.
[0095] It turned out that it is the value which a presentation is expressed with Li1.05nickel0.95O1.95F0.05, and the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) show in the following table 1 when the powder X diffraction which used CuK alpha rays is carried out about the obtained product. Moreover, D50 and specific surface area of said Li1.05nickel0.95O1.95F0.05 powder are shown in the following table 2.
[0096] The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned above Li1.05nickel0.95O1.95F0.05 obtained powder except having used as positive active material was assembled.
[0097] [Example 9] nickel0.83Co0.17 (OH) 2 Spray drying was performed after having dropped the sodium-hydroxide water solution of 3 mol/L so that the mole ratio of Li:

(nickel+Co+B) might be set to 1.02:1, after mixing the cobalt coprecipitation nickel hydroxide powder and tetraboric-acid lithium ($Li_2B_4O_7$) which are expressed so that the mole ratio of B: (nickel+Co) may be set to 0.02:1, and fully mixing. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. The oxygen air current was introduced for the obtained product, and as the oxygen density became 95% or more, after it held, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.

[0098] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is $LiNi_{0.81}Co_{0.17}B_{0.02}O_2$. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said $LiNi_{0.81}Co_{0.17}B_{0.02}O_2$ Powdered D50 and specific surface area are shown in the following table 2.

[0099] Obtained $LiNi_{0.81}Co_{0.17}B_{0.02}O_2$ The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.

[0100] [Example 10] $nickel_{0.83}Co_{0.17}(OH)_2$ Spray drying was performed, after making 3 mol/L lithium-hydroxide water solution distribute the cobalt coprecipitation nickel hydroxide powder and lithium fluoride which are expressed so that the mole ratio of Li:nickel:Co:F may be set to 1.05:0.81:0.17:0.05 and fully mixing. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. The oxygen air current was introduced for the obtained product, and as the oxygen density became 95% or more, after it held, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.

[0101] It turned out that it is the value which a presentation is expressed with $Li_{1.05}nickel_{0.81}Co_{0.17}O_{1.95}F_{0.05}$, and the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) show in the following table 1 when the powder X diffraction which used CuK alpha rays is carried out about the obtained product. Moreover, D50 and specific surface area of said $Li_{1.05}nickel_{0.81}Co_{0.17}O_{1.95}F_{0.05}$ powder are shown in the following table 2.

[0102] The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned above $Li_{1.05}nickel_{0.81}Co_{0.17}O_{1.95}F_{0.05}$ obtained powder except having used as positive active material was assembled.

[0103] [Example 11] $nickel_{0.83}Co_{0.17}(OH)_2$ The cobalt coprecipitation nickel hydroxide powder expressed was distributed so that the mole ratio of Mn: (nickel+Co) might become the manganese nitrate water solution of 3 mol/L with 0.02:1. The sodium-hydroxide water solution of 3 mol/L is dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C. Spray drying was performed after having been dropped so that the mole ratio of Li: (nickel+Co+Mn) might become the obtained product with 1.02:1 about the lithium-hydroxide water solution of 3 mol/L, and fully mixing. It held at the temperature of 700 degrees C for 48 hours, introducing an oxygen air current so that an oxygen density may become 95% or more

about the obtained dry matter. The oxygen air current was introduced for the obtained product, and as the oxygen density became 95% or more, after it held, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.

[0104] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.81Co0.17Mn 0.02O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.81Co0.17Mn 0.02O2 Powdered D50 and specific surface area are shown in the following table 2.

[0105] Obtained LiNi0.81Co0.17Mn 0.02O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.

[0106] [Example 12] nickel0.83Co0.17 (OH) 2 The sodium-hydroxide water solution of 3 mol/L is dropped at the thing which made the manganese nitrate water solution of 3 mol/L distribute the cobalt coprecipitation nickel hydroxide powder, aluminum hydroxide, and tetraboric-acid lithium which are expressed so that the mole ratio of B:aluminum:Mn: (nickel+Co) may be set to 0.02:0.02:0.03:1, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C. Spray drying was performed after having dropped the lithium-hydroxide water solution of 3 mol/L at the obtained product so that the mole ratio of Li: (nickel+Co+Mn+aluminum+B) might be set to 1.02:1, and fully mixing. It held at the temperature of 700 degrees C for 5 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. The oxygen air current was introduced for the obtained product, and as the oxygen density became 95% or more, after it held, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.

[0107] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.77Co0.16Mn0.03aluminum 0.02B0.02O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.77Co0.16Mn0.03aluminum 0.02B0.02O2 Powdered D50 and specific surface area are shown in the following table 2.

[0108] Obtained LiNi0.77Co0.16Mn0.03aluminum 0.02B0.02O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.

[0109] [Example 13] nickel0.83Co0.17 (OH) 2 The sodium-hydroxide water solution of 3 mol/L is dropped at the thing which made the manganese nitrate water solution of 3 mol/L distribute the cobalt coprecipitation nickel hydroxide powder, aluminum hydroxide and tetraboric-acid lithium which are expressed, and lithium fluoride so that the mole ratio of Li:B:aluminum:Mn: (nickel+Co) may be set to 1.05:0.02:0.02:0.03:0.95, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C. Spray drying was performed after having dropped the lithium-hydroxide water solution of 3 mol/L at the obtained product so that the mole ratio of Li: (nickel+Co+Mn+aluminum+B) might be set to 1.05:0.95, and fully mixing. It held at the

temperature of 700 degrees C for 5 hours, introducing an oxygen air current so that an oxygen density may become 95% or more about the obtained dry matter. The oxygen air current was introduced for the obtained product, and as the oxygen density became 95% or more, after it held, heat-treatment was performed at 800 degrees C for 5 hours, pressurizing to 1MPas.

[0110] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is Li1.05nickel0.75Co0.15Mn0.03aluminum0.02B0.02F0.05O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said D50 and specific surface area of Li1.05nickel0.75Co0.15Mn0.03aluminum0.02F0.05O1.95 powder are shown in the following table 2.

[0111] The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned above the obtained Li1.05nickel0.75Co0.15Mn0.03aluminum0.02F0.05O1.95 powder except having used as positive active material was assembled.

[0112] [Example 1 of comparison] nickel0.83Co0.17 (OH) 2 The aluminium nitrate water solution of 1 mol/L was made to distribute the cobalt coprecipitation nickel hydroxide powder and aluminum hydroxide which are expressed so that the mole ratio of aluminum: (nickel+Co) may be set to 0.01:1. The sodium-hydroxide water solution of 3 mol/L was dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C, and the front face was covered with the aluminum hydroxide. after fully mixing the product and lithium hydroxide which were obtained with a ball mill so that the mole ratio of Li: (nickel+Co+aluminum) may be set to 1.02:1, an oxygen density becomes 15% or less 10% or more -- as -- an air air current -- per hour -- heat treatment was performed at the temperature of 800 degrees C for 5 hours, doing 10L installation of.

[0113] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.82 Co0.17aluminum 0.01O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.82 Co0.17aluminum 0.01O2 Powdered D50 and specific surface area are shown in the following table 2.

[0114] Obtained LiNi0.82 Co0.17aluminum 0.01O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.

[0115] [Example 2 of comparison] nickel0.83Co0.17 (OH) 2 The aluminium nitrate water solution of 1 mol/L was made to distribute the cobalt coprecipitation nickel hydroxide powder and aluminum hydroxide which are expressed so that the mole ratio of aluminum: (nickel+Co) may be set to 0.01:1. The sodium-hydroxide water solution of 3 mol/L was dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C, and the front face was covered with the aluminum hydroxide. after fully mixing the product and lithium hydroxide which were obtained with a ball mill so that the mole ratio of Li: (nickel+Co+aluminum) may be set to 1.02:1,

an oxygen density becomes 15% or less 10% or more -- as -- the mixed-gas air current of an argon and oxygen -- per hour -- heat treatment was performed at the temperature of 690 degrees C for 5 hours, doing 10L installation of.

[0116] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.82 Co0.17aluminum 0.01O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.82 Co0.17aluminum 0.01O2 Powdered D50 and specific surface area are shown in the following table 2.

[0117] Obtained LiNi0.82 Co0.17aluminum 0.01O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.

[0118] [Example 3 of comparison] nickel0.83Co0.17 (OH) 2 The aluminium nitrate water solution of 1 mol/L was made to distribute the cobalt coprecipitation nickel hydroxide powder and aluminum hydroxide which are expressed so that the mole ratio of aluminum: (nickel+Co) may be set to 0.01:1. The sodium-hydroxide water solution of 3 mol/L was dropped at this, and it was made to react continuously, holding and agitating in temperature of 40-60 degrees C, and the front face was covered with the aluminum hydroxide. after fully mixing the product and lithium hydroxide which were obtained with a ball mill so that the mole ratio of Li: (nickel+Co+aluminum) may be set to 1.02:1, an oxygen density becomes 15% or less 10% or more -- as -- the mixed-gas air current of an argon and oxygen -- per hour -- heat treatment was performed at the temperature of 650 degrees C for 5 hours, doing 10L installation of.

[0119] When the powder X diffraction which used CuK alpha rays was carried out about the obtained product, a presentation is LiNi0.82 Co0.17aluminum 0.01O2. It was expressed and it turned out that the peak intensity ratio I (104) / I (003), FWHM (003) and FWHM (104), and the half-peak-width ratios FWHM (003)/FWHM (104) are the values shown in the following table 1. Moreover, said LiNi0.82 Co0.17aluminum 0.01O2 Powdered D50 and specific surface area are shown in the following table 2.

[0120] Obtained LiNi0.82 Co0.17aluminum 0.01O2 The cylindrical non-aqueous-solvent rechargeable battery shown in drawing 1 which was the same as that of an example 1, and mentioned powder above except having used as positive active material was assembled.

[0121] after charging to 4.2V by 400mA of constant current about the rechargeable battery of examples 1-13 and the examples 1-3 of a comparison -- further -- it charged so that the total charging time might turn into 8 hours by the constant voltage of 4.2V, and the discharge capacity when discharging to 2.7V by constant current (400mA, 2000mA, and 4000mA) was measured. The capacity maintenance factor at the time of 2000mA discharge to the capacity at the time of 400mA discharge and the capacity maintenance factor at the time of 4000mA discharge to the capacity at the time of 400mA discharge are computed, and the result is shown in the following table 3.

[0122] after [moreover,] charging to 4.2V by 400mA of constant current about the rechargeable battery of examples 1-13 and the examples 1-3 of a comparison -- further -- after charging so that the total charging time may turn into 8 hours by the constant voltage of 4.2V, while acting as the monitor of cell voltage and the temperature of a cell

container front face -- a nail with a diameter of 2.5mm -- 136cm/second in rate -- a cell container -- the core was made to penetrate mostly The highest attainment temperature at that time is measured, and it writes together to the following table 3.
[0123]
[Table 1]

	活物質の組成	I(104)/I(003)	FWHM (003) (°)	FWHM (104) (°)	FWHM(003)/FWHM(104)
実施例1	$LiNiO_2$	0.78	0.132	0.151	0.874
実施例2	$LiNi_{0.83}Co_{0.17}O_2$	0.66	0.136	0.167	0.814
実施例3	$LiNi_{0.81}Co_{0.17}Al_{0.02}O_2$	0.72	0.135	0.162	0.833
実施例4	$LiNi_{0.827}Co_{0.17}Al_{0.003}O_2$	0.68	0.125	0.166	0.753
実施例5	$LiNi_{0.827}Co_{0.17}Al_{0.003}O_2$	0.66	0.110	0.130	0.846
実施例6	$LiNi_{0.827}Co_{0.17}Al_{0.003}O_2$	0.77	0.151	0.182	0.830
実施例7	$LiNi_{0.8}Mn_{0.2}O_2$	0.74	0.147	0.188	0.875
実施例8	$Li_{1.05}Ni_{0.95}O_{1.95}F_{0.05}$	0.73	0.142	0.167	0.860
実施例9	$LiNi_{0.81}Co_{0.17}B_{0.02}O_2$	0.67	0.132	0.148	0.892
実施例10	$Li_{1.05}Ni_{0.81}Co_{0.17}O_{1.95}F_{0.05}$	0.74	0.144	0.163	0.883
実施例11	$LiNi_{0.81}Co_{0.17}Mn_{0.02}O_2$	0.77	0.148	0.168	0.881
実施例12	$LiNi_{0.77}Co_{0.16}Mn_{0.03}Al_{0.02}B_{0.02}O_2$	0.75	0.145	0.167	0.868
実施例13	$Li_{1.05}Ni_{0.75}Co_{0.15}Mn_{0.03}Al_{0.02}F_{0.05}O_{1.95}$	0.73	0.148	0.174	0.851
比較例1	$LiNi_{0.82}Co_{0.17}Al_{0.01}O_2$	0.76	0.102	0.137	0.744
比較例2	$LiNi_{0.82}Co_{0.17}Al_{0.01}O_2$	0.78	0.152	0.162	0.938
比較例3	$LiNi_{0.82}Co_{0.17}Al_{0.01}O_2$	0.92	0.237	0.331	0.716

[0124]
[Table 2]

	D50 (μm)	比表面積 (m^2/g)
実施例1	10.2	0.73
実施例2	10.0	0.65
実施例3	10.0	0.32
実施例4	9.8	0.51
実施例5	9.8	0.53
実施例6	5.1	1.22
実施例7	10.0	0.89
実施例8	10.2	0.90
実施例9	10.0	0.72
実施例10	10.2	0.87
実施例11	10.0	1.00
実施例12	10.2	0.71
実施例13	5.0	1.35
比較例1	10.0	0.18
比較例2	10.0	0.55
比較例3	4.8	2.11

[0125]
[Table 3]

	2000mA 容量維持率 (%)	4000mA 容量維持率 (%)	平均放電電圧 (V)	釘刺し時 最高到達温度 (℃)	破裂・発火 の有無
実施例1	92	80	3.67	102	なし
実施例2	95	82	3.64	89	なし
実施例3	96	83	3.65	92	なし
実施例4	98	83	3.68	83	なし
実施例5	91	78	3.64	88	なし
実施例6	90	74	3.65	92	なし
実施例7	90	71	3.62	78	なし
実施例8	88	69	3.61	97	なし
実施例9	88	70	3.64	96	なし
実施例10	87	66	3.62	83	なし
実施例11	85	67	3.63	85	なし
実施例12	84	65	3.61	94	なし
実施例13	83	62	3.62	82	なし
比較例1	67	35	3.56	499	あり
比較例2	73	43	3.57	459	あり
比較例3	61	32	3.48	480	あり

[0126] The non-aqueous-solvent rechargeable battery of the examples 1-13 equipped with the positive electrode which contains the lithium nickel system multiple oxide which fills (1) type (half-peak-width ratio) and (2) types (peak intensity ratio) which were mentioned above so that clearly from Table 1 - 3 as an active material can have high average discharge voltage, can control the capacity fall at the time of discharging by the high current, can suppress generation of heat of the cell in a peg test, and is understood that safety is high.
[0127] On the other hand, although a peak intensity ratio fills said range, it turns out that the rechargeable battery of the examples 1-3 of a comparison equipped with the positive electrode which contains the lithium nickel system multiple oxide from which a half-peak-width ratio separates from said range as an active material has low capacity and average discharge voltage at the time of discharging by the high current compared with the rechargeable battery of examples 1-13, temperature moreover rises to about 500 degrees C in a peg test, and a burst and ignition are produced.
[0128] In addition, a 3 electrode glass cell is assembled using the positive electrode of the rechargeable battery of examples 4 and 9, and the counter electrode and reference pole which consist of a metal lithium. Charge-and-discharge cycle trial (it carries out by the constant current of 1 mA/cm2 to 4.2V) [Charge;] Carry out after reaching 4.2V until a current becomes 1/10 or less by the constant voltage. discharge; -- until it reaches 3V by the constant current of 1 mA/cm2 -- carrying out -- after 50 cycle ****** When the positive electrode was taken out from the glass cell and the powder X diffraction using CuK alpha rays was carried out, about the positive active material of the rechargeable

battery of an example 4, I (003) was the peak intensity ratios I (104)/0.29, and FWHM (104) was the half-peak-width ratios FWHM (003)/0.824. On the other hand, about the positive active material of the rechargeable battery of an example 9, I (003) was the peak intensity ratios I (104)/0.29, and FWHM (104) was the half-peak-width ratios FWHM (003)/0.899.

[0129] Moreover, the evaluation same also about the positive active material which consists of a multiple oxide which permuted some nickel of LiNiO2 by B, aluminum, or Li as an example was performed, and it checked that the same effectiveness as an example was acquired.

[0130]

[Effect of the Invention] The non-aqueous-solvent rechargeable battery whose safety at the time of the abnormalities in a cell according to this invention whose discharge voltage was high and was excellent in the high current charge-and-discharge property as explained in full detail above, and improved can be offered.